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CASE 247

PATENT SPECIFICATION

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(54) ESTERS AND THEIR USE AS MALODOR COUNTERACTANTS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis Missouri 63166, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the art of treatment of offensive odors, more particularly, to compositions and methods to counteract certain malodors.

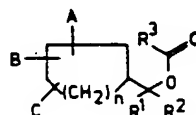
Heretofore a major effort in the art of perfumery has been directed to providing means of treating odors that are offensive to the human sense of smell. Such odors encompass a variety of odors such as bathroom-odor, kitchen-odor, body-odor, and cigar smoke-odor. Many products have been developed in an attempt to overcome these odors. So-called "room fresheners" or "room deodorants" are illustrative of such products.

In general these products have provided a masking effect by one of two mechanisms. The maskant fragrance is provided either to suppress the offensive odor by providing a more pleasing aroma in large quantities or by providing an aroma that blends with the offensive odor to provide a different and more desirable aroma. Unfortunately, in both instances a large amount of fragrance must be utilized which in itself often proves to be offensive. Furthermore, the offensive odor is usually still detectable at the levels of maskant fragrances that are reasonably tolerable. Accordingly, compositions and methods for counter-acting such offensive odors which would substantially eliminate such odors without the above-noted disadvantages are particularly desirable.

Particularly noxious odors are caused by compounds which have a pronounced tendency to either donate or accept protons. Such compounds will hereinafter be referred to as "malodors". They include the olfactory notorious classes of lower carboxylic acids, thiols, thiophenols, phenols, lower amines, phosphines and arsines.

The present invention provides compounds and compositions which are especially useful in view of their ability to counteract malodors. Furthermore, novel methods are provided, i.e. the use of such compounds and compositions to counteract malodors. Still further, certain of these compounds are novel.

The compounds which exhibit this surprising ability to counteract malodors are represented by the following structural formula



(I)

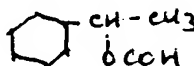
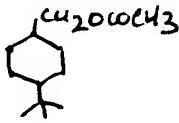
wherein

n is an integer of from 1 to 4,

A, B and C each independently represent hydrogen, or an alkyl group having from 1 to 5 carbon atoms, each such alkyl group, when there are more than one, being attached to a different carbon atom of the ring, provided that the sum of the carbon atoms in A, B and C is no more than 7,

R¹ and R² each independently represent hydrogen or an alkyl group having from 1 to 5 carbon atoms or R¹ and R² taken together represent $-(CH_2)_m-$ wherein m is an integer of from 2 to 6, provided that when both R¹ and R²

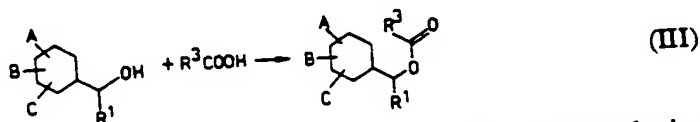
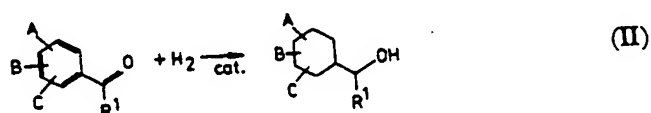
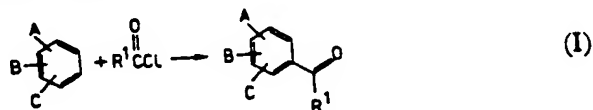
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represent hydrogen, (a) each of A, B and C represents hydrogen, or (b) A represents tert-butyl and B and C each represent hydrogen, R³ represents hydrogen or an alkyl group having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R¹ or R² plus R³ is no more than 10.

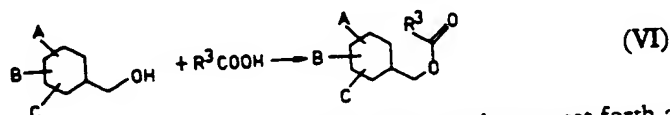
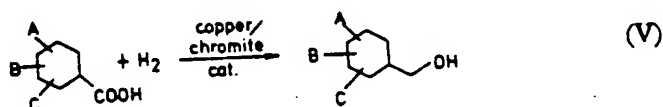
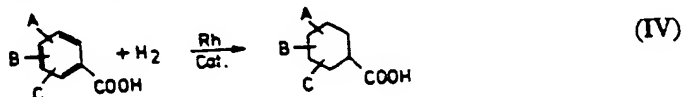
The term "counteract" as used herein means the effect on the human sense of smell and/or the malodor resulting in alleviating the offensiveness of the malodor to the human sense of smell. It is not intended that this term may be limited to any particular mechanism by which such a result may be obtained.

The compounds useful in this invention wherein n is 2 and R¹ is alkyl, can be prepared as illustrated by the following equations:



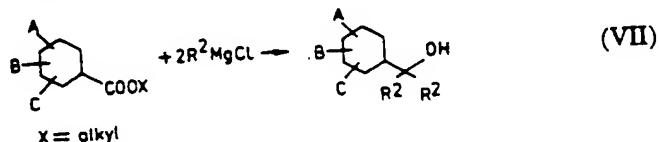
In the above equations, A, B, C and R³ have the same meanings as set forth above. As shown in equation (I) a substituted or unsubstituted benzene is acylated, preferably under Friedel-Crafts conditions, with an acyl chloride to form the corresponding phenyl-alkyl ketone. As shown in equation (II) this phenyl-alkyl ketone is hydrogenated over a suitable catalyst, preferably a rhodium metal-containing to form the corresponding alkylated cyclohexylmethanol. (Certain of the alcohols obtainable in this way are new compounds which are described and claimed in our British Patent Specification 655/78) (Serial No. 1,545,563). Esterification of this alcohol with an appropriate carboxylic acid forms the desired esters as shown in equation (III).

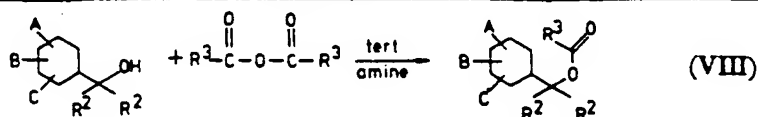
The compounds wherein n is 2 and both R¹ and R² are hydrogen can be prepared as illustrated by the following equations:



In the above equations, A, B, C and R³ have the same meanings as set forth above. As shown in equation (IV) a substituted or unsubstituted benzoic acid is first hydrogenated over a suitable rhodium catalyst to the corresponding hexahydrobenzoic acid which is then hydrogenated (equation (V)) to form the corresponding cyclohexylmethanol. This alcohol can then be esterified, as shown in equation (VI), with an appropriate carboxylic acid to form the desired esters.

The compounds wherein n is 2 and both R¹ and R² are the same alkyl can be prepared as illustrated by the following equations:

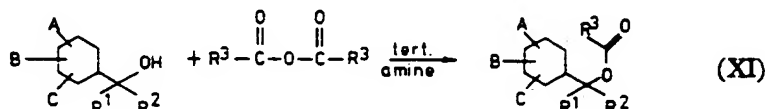
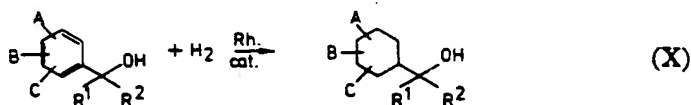
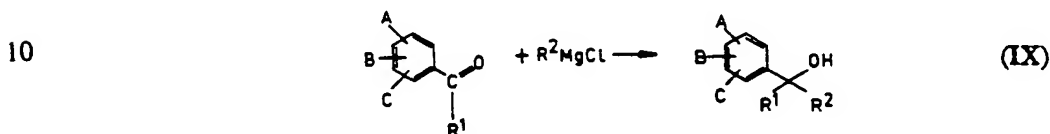




In the above equations, A, B, C and R³ have the same meanings as set forth above.

As shown in equation (VII) an alkyl ester of a substituted or unsubstituted hexahydrobenzoic acid is reacted with an alkyl magnesium chloride to form the corresponding tertiary alcohol. This alcohol is esterified, as shown in equation (VIII), by reaction with the anhydride of an appropriate carboxylic acid in the presence of a tertiary amine, such as triethylamine, to form the desired ester.

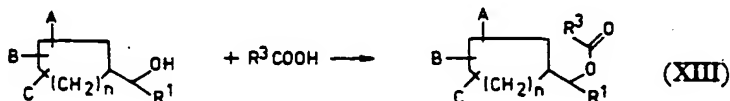
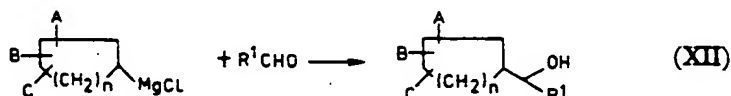
The compounds wherein n is 2 and R¹ and R² are different alkyls can be prepared as illustrated by the following equations:



In the above equations, A, B, C and R³ have the same meanings as set forth above.

As shown in equation (IX), a substituted or unsubstituted phenylalkyl ketone is reacted with an alkyl magnesium chloride to form the corresponding tertiary alcohol which is hydrogenated (equation (X)) over a suitable rhodium catalyst to the corresponding cyclohexyl alcohol. This alcohol is esterified, as shown in equation (XI), by reaction with the anhydride of an appropriate carboxylic acid in the presence of a tertiary amine, such as triethyl amine to form the desired ester.

The compounds useful in this invention wherein n is 1, 3 or 4 can be prepared as illustrated by the following equations:



In the above equations, A, B, C and R³ have the same meanings as set forth above.

As shown in equation (XII) a substituted or unsubstituted cycloalkyl magnesium chloride and an appropriate aldehyde are reacted to form the corresponding cycloalkyl alcohol which is esterified as shown in equation (XIII) to the desired ester.



In the above equation, A, B and C have the same meanings as set forth above and R¹ and R² are alkyl.

As shown in equation (XIV) a substituted or unsubstituted cycloalkyl magnesium chloride is reacted with an appropriate ketone to form the corresponding cycloalkyl tertiary alcohol which can be esterified by reaction with the anhydride of an appropriate

4
carboxylic acid in the presence of a tertiary amine, such as triethylamine, to form the desired ester.

5 The compounds of the above formula wherein R^1 and R^2 taken together represent $-(CH_2)_m-$ can be prepared by first reacting a magnesium chloride of an appropriate substituted or unsubstituted cycloalkyl with an appropriate cycloalkanone to form a tertiary alcohol, wherein the substituted or unsubstituted cycloalkyl group is attached to the same carbon atom as the hydroxyl group, followed by an esterification reaction with the anhydride of an appropriate carboxylic acid substantially as shown in equation (XI).

10 The instant compounds are capable of effectively counteracting malodors when utilized in small quantities and in many different mediums. For instance, use in room fresheners or room deodorants in the form of aerosols (sprays, etc.), liquids (wick type), solids (wax bases as in pomander, plastics, etc.), powders (sachets, dry sprays) and gels (solid gel sticks) are particularly preferred. Other illustrative uses are in clothes deodorants as applied by washing machine applications such as in detergents, powders, liquids, whiteners or fabric softeners or by other applications such as closet blocks, closet aerosol sprays, or clothes storage areas or in dry cleaning to overcome residual solvent notes on clothes; in bathroom accessories such as paper towels, bath- room tissues, sanitary napkins, towellets, disposable wash cloths, disposable diapers, and diaper pail deodorants; in cleansers such as disinfectants and toilet bowl cleaners; in cosmetic products such as antiperspirant and underarm deodorants, general body deodorants in the form of powders, aerosols, liquids or solid, or hair care products such as hair sprays, conditioners, rinses, hair colors and dyes, permanent waves, depilatories, hair straighteners, hair groom applications such as pomade, creams and lotions, medicated hair care products containing such ingredients as selenium sulfide, coal tar or salicylates, or shampoos, or foot care products such as foot powders, liquids or colognes, after shaves and body lotions, or soaps and synthetic detergents such as bars, liquids, foams or powders; in odor control such as during manufacturing processes, such as in the textile finishing industry and the printing industry (inks and paper); in effluent control such as in processes involved in pulping, stock yard and meat processings, sewage treatment, or garbage disposal, or in product odor control as in textile finished goods, rubber finished goods or car fresheners; in agricultural and pet care products such as dog and hen house effluents, and domestic animal and pet care products such as deodorants, shampoo or cleaning agents, or animal litter material and in large scale closed air systems such as auditoria, and subways and transport systems.

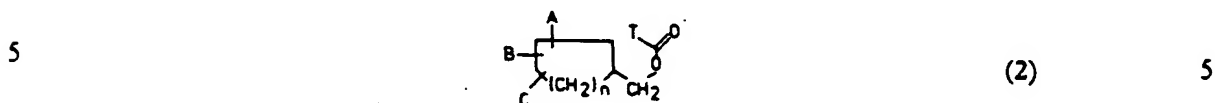
35 Thus it will be seen that the composition of the invention is usually one in which the malodor-counteractant is present together with a carrier by means of which or from which the malodor-counteractant can be introduced into the atmosphere containing the malodor. For example the carrier can be an aerosol propellant such as a chlorofluoro-methane, or a solid such as a wax, plastics material, rubber, inert powder or gel. In a wick-type air freshener, the carrier is a substantially odorless liquid of low volatility. In several applications, a composition of the invention contains a surface active agent or a disinfectant, while in others, the malodor counteractant is present on a fibrous substrate. In many compositions of the invention there is also present a fragrance component which imparts a fragrance to the composition, and often includes a plurality, for example at least three, ingredients, for instance lavandin abrialis oil, amyl salicylate, geraniol, isopulegol, musk xylol, terpinyl acetate or ylang ylang oil. The amount of the fragrance component present in a composition of the invention containing such a component is generally at least equal to that of the malodor-counteractant, and preferably the amount of the former exceeds that of the latter such that the weight ratio of fragrance component to malodor-counteractant is within the range 1.1:1 to 20:1, and more specifically within the range 2:1 to 15:1.

40 The amount of the odor-counteractant to be utilized depends, in general, on the particular malodor involved and its concentration in the air containing it and on other variables such as the medium in which the compound is used and the temperature, humidity and air circulation. An amount effective to counteract the malodor should be used. In general, the compounds are effective when present in air (containing the malodor) at levels are low as about 0.01 mg./cubic meter of air. Any concentration above this amount will generally be effective. However, from a practical point of view, more than about 1 mg./cubic meter of air is probably unnecessary even with the most offensive and concentrated malodors.

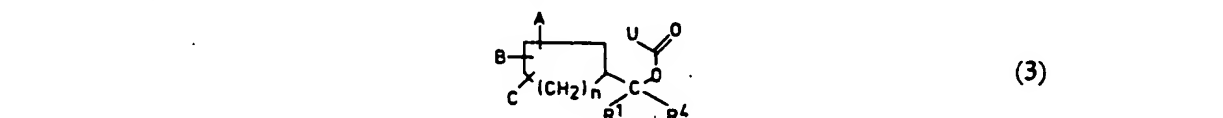
55 Similarly the concentration of the malodor-counteractant in a composition of the invention will depend on the type of composition and the way it is to be used. For

example in an aerosol formulation, the concentration of malodor-counteractant can be for instance from 0.02 to 0.20 percent of the total weight of the composition.

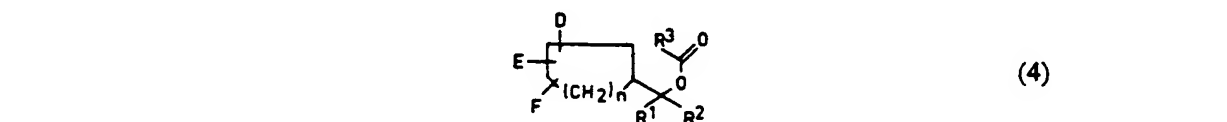
Novel compounds useful in the present invention are represented by the following structural formulae:



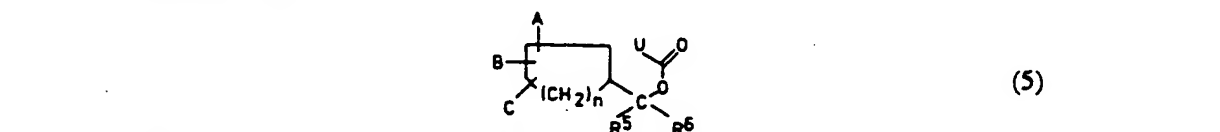
wherein n is an integer from 1 to 4, A, B and C each represent hydrogen, and T represents an alkyl group having from 3 to 6 carbon atoms;



wherein n, A, B, C and R¹ have the same meanings as set forth above, R⁴ represents an alkyl group having from 1 to 5 carbon atoms, or R¹ and R⁴ taken together represent $-(CH_2)_m-$ wherein m has the same meaning as set forth above, and U represents hydrogen or an alkyl group having from 2 to 6 carbon atoms; provided that the sum of the larger number of carbon atoms in either R¹ or R⁴ plus U is no more than 10;



20 wherein n, R¹, R² and R³ have the same meanings as set forth above and D, E and F each independently represent hydrogen or an alkyl group having from 2 to 5 carbon atoms, each such alkyl group, when there are more than one, being attached to a different carbon atom of the ring, provided that at least one of D, E or F is not hydrogen, that when both R¹ and R² represent hydrogen D represents t-butyl and E and F each represent hydrogen and that the sum of the carbon atoms in D, E and F is no more than 7;



wherein n, A, B, C and U have the same meanings as set forth above, and R⁵ and R⁶ each independently represent an alkyl group having from 1 to 5 carbon atoms or R⁵ and R⁶ taken together represent $-(CH_2)_m-$ wherein m has the same meaning as set forth above, provided that the sum of the larger number of carbon atoms in either R⁵ or R⁶ plus U is no more than 10.

Particularly preferred compounds useful in the instant invention are those wherein n is 2, i.e., where the ring structure is cyclohexyl. A particularly preferred compound is 1-cyclohexyl-1-ethyl n-butyrate.

Other illustrative compounds useful in the present invention are:

- cyclohexylmethyl propionate
- cyclohexylmethyl isobutyrate
- cyclohexylmethyl n-butyrate
- 35 cis/trans-4-tert.butylcyclohexylmethyl acetate
- 1-cyclohexyl-1-ethyl formate
- 1-cyclohexyl-1-ethyl acetate
- 1-cyclohexyl-1-ethyl-propionate
- 1-cyclohexyl-1-ethyl isobutyrate
- 40 1-cyclohexyl-1-propyl acetate
- 1-cyclohexyl-1-propyl n-butyrate
- 1-cyclohexyl-2-methyl-1-propyl acetate
- 1-cyclohexyl-2-methyl-1-propyl n-butyrate
- 1-cyclohexyl-1-butyl acetate
- 45 1-cyclohexyl-1-butyl n-butyrate
- 1-cyclohexyl-1-pentyl acetate
- 1-cyclohexyl-1-pentyl n-butyrate

8.5 g=80% of cis/trans-4-tert.butylcyclohexylmethyl acetate which is a colorless, fragrant liquid with a purity of 99.97%. GLC did not resolve the peaks, but the major component was eluted first.

Example 5 (Comparative)

cis/trans-4-Methylcyclohexylmethyl Acetate

A mixture of 6.4 g. (0.05 moles) of cis/trans-4-methylcyclohexylmethanol and 5.5 g. (0.055 moles) of acetic anhydride was reacted and the product was recovered as described in Example 4. The product, a colorless fragrant liquid, had b.p. 46—48°C./0.2 mm., $n_D^{25}=1.4444$. Yield 7.6 g. (89.3%). Purity 99.85% of cis/trans-4-methylcyclohexylmethyl acetate. GLC did not separate the isomers on a 6 ft. LAC column.

Example 6 (Comparative)

cis/trans-4-Isopropylcyclohexylmethyl Acetate

To a mixture of 7.8 g. (0.05 moles) cis/trans-4-isopropylcyclohexylmethanol and 5.5 g. (0.055 moles) of acetic anhydride were added a few crystals of p-toluene sulfonic acid and the reaction run and the product was recovered as described in Example 4. The product, a colorless fragrant liquid, had b.p. 85°C./1 mm., $n_D^{25}=1.4520$. Yield 9.0 g. (90.8%) of 99.9% purity of cis/trans-4-isopropylcyclohexylmethyl acetate by GLC. No separation of stereoisomers on a LAC column was observed.

Example 7

1-Cyclohexyl-1-Ethyl Formate

A mixture of 12.8 g. (0.1 moles) 1-cyclohexyl-1-ethanol and 13.8 g. (0.3 moles) formic acid was refluxed for two hours and then cooled to room temperature. It was poured in 200 ml. cold water, the organic material extracted in ether and the ether extract washed thoroughly with water, sodium bicarbonate, water and brine and dried over molecular sieves. 15.4 g. crude product of 97.9% purity was recovered—major impurity is residual solvent. The crude product was distilled through a short Vigreux-column. The product is a mobile, colorless liquid, b.p. 94°C./16 mm., $n_D^{25}=1.4437$. Yield 13.6 g.=87.1%, purity 99.2% (by GLC) of 1-cyclohexyl-1-ethyl formate.

Example 8

1-Cyclohexyl-1-Ethyl Acetate

A mixture of 25.6 g. (0.2 moles) 1-cyclohexyl-1-ethanol and 22.0 g. acetic anhydride (0.22 moles) containing 100 mg. p-toluene sulfonic acid was warmed to 50°C. A strongly exothermic reaction occurred which was allowed to proceed freely. A maximum temperature of 123°C. was reached. After standing at room temperature the reaction mixture was diluted with the same volume of ether and poured into 300 ml. cold water. The organic layer was separated, thoroughly washed with water (4×50 ml.), sodium bicarbonate solution, water again and finally brine. The solvent was evaporated on a rotary evaporator to give 33.5 g. of crude product, purity 98.76% by GLC. Distillation through a short Vigreux-column afforded 30.8 g. of pure product, b.p. 85°C./10 mm., $n_D^{24}=1.4445$, colorless liquid of fruity-floral-woody odor with a touch of an animal note. NMR analysis confirmed the product as 1-cyclohexyl-1-ethyl acetate.

Example 9

1-Cyclohexyl-1-Ethyl Propionate

To a mixture of 12.8 g. (0.1 moles) 1-cyclohexyl-1-ethanol and 14.3 g. (0.11 moles) propionic anhydride was added 100 mg. p-toluene sulfonic acid and the mixture left at room temperature for 18 hours. Then 0.2 ml. water was added and the mixture left one more hour at room temperature and then poured in 200 ml. cold water. The organic layer was separated, the aqueous layer extracted once with ether and the combined organic material washed with water, sodium bicarbonate, water and finally brine. After drying over molecular sieves afforded 18.6 g. of crude material, $n_D^{25}=1.4442$ which was practically pure. Distillation through a short Vigreux-column afforded the product, b.p. 98.5°C./10 mm., $n_D^{24}=1.4446$, yield 15.5 g.=84.1%. Purity 99.7% by GLC of 1-cyclohexyl-1-ethyl propionate having a fatty, dirty and oily odor.

Example 10

1-Cyclohexyl-1-Ethyl Isobutyrate

A solution of 25.6 g. (0.2 moles) 1-cyclohexyl-1-ethanol and 19.4 g. (0.22 moles) isobutyric acid in 100 ml. benzene, containing 2 g. p-toluene sulfonic acid, was heated to gentle reflux-water distilled at a reasonable rate. After refluxing overnight 3.6 ml. of water were collected. The mixture was extracted with excess cold saturated sodium

bicarbonate solution, washed with water and brine and evaporated on a rotary evaporator to give 38.1 g. of a colorless fragrant liquid, $n_D^{25}=1.4435$. GLC=91.94% product and 6.91% low boilers. The product was purified by distillation through a Holtzmann-column. After a small forerun (discarded) the product was obtained as a colorless, fragrant liquid, b.p. $56^\circ\text{C./0.3 mm.}$, $n_D^{25}=1.4420$, yield 33.5 g. (83.2%). NMR analysis confirmed the product as 1-cyclohexyl-1-ethyl isobutyrate.

Example 11

1-Cyclohexyl-1-Ethyl n-Butyrate

To a mixture of 12.8 g. (0.1 moles) 1-cyclohexyl-1-ethanol and 9.7 g. (0.11 moles, 10% excess) n-butyric acid in 50 ml. benzene was added 1 g. p-toluene sulfonic acid and with stirring refluxed gently overnight. 1.8 ml. (calculated amount) water were collected in a trap. The benzene solution was allowed to cool to room temperature, then washed with sodium bicarbonate solution, water and brine, and evaporated on a rotary evaporator to give 18.3 g. of crude ester, $n_D^{24}=1.4462$, purity 95.9%. Distillation through a short Vigreux-column gave the pure product, b.p. $97.5^\circ\text{C./4 mm.}$, $n_D^{25}=1.4456$, yield 15.4 g. (77.7%), purity by GLC 99.7% of 1-cyclohexyl-1-ethyl n-butyrate which is a colorless, mobile fragrant liquid.

Example 12

1-Cyclohexyl-1-Propyl Acetate

A mixture of 1.42 g. 1-cyclohexyl-1-propanol and 11.2 g. acetic anhydride containing 100 mg. p-toluene sulfonic acid was left at room temperature for 24 hours. It was then poured in excess (200 ml.) water, the organic material extracted with ether and the ether layer washed thoroughly with water and sodium bicarbonate solution and brine and dried over molecular sieves. 15.8 g. of crude product, $n_D^{25}=1.4456$ was recovered. It was distilled through a short Vigreux-column to give two fractions:

b.p. 69°C./2 mm. , $n_D^{25}=1.4456$ 1.6 g. (Fraction 1)
b.p. 69°C./2 mm. , $n_D^{25}=1.4456$ 13.5 g. (Fraction 2)

Fraction 2 was 99.6% pure, by GLC, 1-cyclohexyl-1-propyl acetate.

Example 13

1-Cyclohexyl-1-Propyl n-Butyrate

A solution of 14.2 g. (0.1 moles) 1-cyclohexyl-1-propanol and 9.7 g. n-butyric acid (10% excess) in 50 ml. benzene, containing 0.25 ml. concentrated sulfuric acid was heated to reflux and water collected in a Dean-Stark trap. 13.1 g. (61.7%) of crude product, $n_D^{25}=1.4508$ were recovered. Two low boiling minor peaks suggest that considerable dehydration had occurred. Distillation of the crude product through a short Vigreux-column afforded two fractions

b.p. $23-76^\circ\text{C./0.7 mm.}$, $n_D^{25}=1.4518$ 3.8 g. (Fraction 1)
b.p. $72^\circ\text{C./0.4 mm.}$, $n_D^{25}=1.4470$ 8.3 g. (Fraction 2)

Fraction 2, 1-cyclohexyl-1-propyl n-butyrate, a colorless mobile liquid, had a weak fruity, prune-like odor.

Example 14

1-Cyclohexyl-2-Methyl-1-Propyl Acetate

To a mixture of 15.6 g. (0.1 moles) 1-cyclohexyl-2-methyl-1-propanol and 11.2 g. (0.11 moles) acetic acid was added 100 mg. p-toluene sulfonic acid and the mixture left at room temperature overnight. Then 1 g. sodium acetate and 1 ml. water was added, the mixture stirred for one hour and poured into 150 ml. water. The organic layer was separated, the aqueous layer extracted with 2×50 ml. ether and the combined extracts and organic layer washed thoroughly with water, sodium bicarbonate solution, water and brine. After drying over molecular sieves overnight 17.4 g. of crude product, $n_D^{25}=1.4482$, was recovered which was practically pure. Distillation through a Vigreux-column gave the pure product, b.p. $79^\circ\text{C./2.9 mm.}$, $n_D^{25}=1.4477$ which was 1-cyclohexyl-2-methyl-1-propyl acetate.

Example 15

1-Cyclohexyl-2-Methyl-1-Propyl n-Butyrate

To a solution of 17.2 g. (0.11 moles) 1-cyclohexyl-2-methyl-1-propanol and 8.7 g. (0.11 moles) pyridine in 100 ml. anhydrous ether, chilled in an ice bath, was added with stirring a solution of 11.72 g. (0.11 moles) butyryl chloride in 20 ml. anhydrous

ether at such a rate as to keep the temperature at 4–6°C. After complete addition the ice bath was removed and stirring at room temperature continued for several hours. Enough ice water was added to dissolve the precipitate and the organic layer separated. It was washed thoroughly with cold 3% hydrochloric acid, water, sodium bicarbonate solution, water and brine and dried over molecular sieves for 18 hours. 19.9 g. of crude material was recovered which was distilled through a short Vigreux-column to give the product 1-cyclohexyl-2-methyl-1-propyl n-butyrate, b.p. 91°C./0.8 mm., $n_D^{25}=1.4507$. This compound has a tabac-type odor.

Example 16

1-Cyclohexyl-1-Butyl Acetate

15.6 g. (0.1 moles) of 1-cyclohexyl-1-butanol were acetylated with 11.2 g. (0.11 moles) acetic anhydride and 100 mg. p-toluene sulfonic acid and recovered as described in Example 14. 16.9 g. (85.2%) of crude product, $n_D^{24}=1.4472$ was obtained which was practically pure. Distillation through a short Vigreux-column afforded two fractions

b.p. 52–60°C./0.5 mm., $n_D^{22}=1.4484$, 1.2 g. (Fraction 1)
b.p. 60°C./0.5 mm., $n_D^{22}=1.4484$, 14.6 g. (Fraction 2)

Both fractions were of 99+ % purity, by GLC, 1-cyclohexyl-1-butyl acetate. This compound has an earthy, woody, spicy, rooty, vetiver odor.

Example 17

1-Cyclohexyl-1-Butyl n-Butyrate

Using a procedure similar to that used in Example 15, 1-cyclohexyl-1-butanol was reacted with n-butyryl chloride to form 1-cyclohexyl-1-butyl n-butyrate, b.p. 85°C./0.75 mm., $n_D^{23}=1.4490$.

Example 18

1-Cyclohexyl-1-Pentyl Acetate

17.0 g. (0.1 moles) of 1-cyclohexyl-1-pentanol were acetylated with 11.2 g. (0.11 moles) acetic anhydride and 100 mg. p-toluene sulfonic acid and recovered as described in Example 14. 20.0 g. of crude product, $n_D^{22}=1.4495$ were obtained, practically pure. This material had a b.p. 96°C./0.9 mm. and $n_D^{25}=1.4485$ 1-cyclohexyl-1-pentyl acetate.

Example 19

1-Cyclohexyl-1-Pentyl n-Butyrate

Using a procedure similar to that used in Example 15, 1-cyclohexyl-1-pentanol was reacted with butyryl chloride to form 1-cyclohexyl-1-pentyl n-butyrate, b.p. 100°C./2.9 mm., $n_D^{23}=1.4508$.

Example 20

cis/trans-1-(2'-Methylcyclohexyl)-1-Ethyl Acetate

A mixture of 14.2 g. (0.1 moles) cis/trans-1-(2-methylcyclohexyl)-1-ethanol, 11.2 g. (0.11 moles) acetic anhydride and 100 mg. p-toluene sulfonic acid was reacted and recovered as described in Example 14. 16.4 g. of crude product, 1-(2'-methylcyclohexyl)-1-ethyl acetate, $n_D^{22}=1.4497$, was obtained as a colorless, fragrant liquid. GLC showed this to be a mixture of one major and two minor components. Distillation through a short Vigreux-column afforded the same mixture, b.p. 97°C./0.9 mm., $n_D^{25}=1.4435$.

Example 21

cis/trans-1-(2'-Methylcyclohexyl)-1-Ethyl n-Butyrate

Using a procedure similar to that used in Example 15, 1-(2'-methylcyclohexyl)-1-ethanol was reacted with n-butyryl chloride to form 1-(2'-methylcyclohexyl)-1-ethyl n-butyrate, b.p. 75°C./0.6 mm., $n_D^{25}=1.4517$.

Example 22

cis/trans-1-(3'-Methylcyclohexyl)-1-Ethyl Acetate

14.2 g. (0.1 moles) of cis/trans-1-(3'-methylcyclohexyl)-1-ethanol, 11.2 g. (0.11 moles) of acetic anhydride and 100 mg. p-toluene sulfonic acid were reacted and the product, cis/trans-1-(3'-methylcyclohexyl)-1-ethyl acetate, was recovered as described in Example 14. 17.0 g. of material, practically pure by GLC, were obtained. The product has a b.p. 57°C./0.9 mm., $n_D^{25}=1.4435$.

Example 23

cis/trans-1-(3'-Methylcyclohexyl)-1-Ethyl n-Butyrate

Using a procedure similar to that used in Example 15, 1-(3'-methylcyclohexyl)-1-

ethanol was reacted with n-butyryl chloride to form 1-(3'-methylcyclohexyl)-1-ethyl n-butyrate, b.p. 93°C./3.5 mm., $n_D^{25}=1.4448$.

Example 24

cis/trans-1-(4'-Methylcyclohexyl)-1-Ethyl Acetate

To a mixture of 12.8 g. (0.09 moles) cis/trans-1-(4'-methylcyclohexyl)-1-ethanol and 10.2 g. (0.1 moles) acetic anhydride was added 100 mg. p-toluene sulfonic acid and the solution left at room temperature overnight. The resulting mass was poured into 100 ml. of water and washed thoroughly and subsequently with water, sodium bicarbonate solution, water and brine, dried over molecular sieves. 14.9 g. of crude material was recovered, $n_D^{25}=1.4434$, purity 99.50% of cis/trans-1-(4'-methylcyclohexyl)-1-ethyl acetate. This material was distilled through a short Vigreux-column to give product, b.p. 42—43°C./0.3 mm., $n_D^{25}=1.4433$, purity 99.82%. Yield 13.2 g.

Example 25

cis/trans-1-(4'-Methylcyclohexyl)-1-Ethyl Isobutyrate

To a mixture of 12.8 g. (0.09 moles) cis/trans-1-(4'-methylcyclohexyl)-1-ethanol and 14.2 g. isobutyric anhydride was added 100 mg. p-toluene sulfonic acid and the solution left at room temperature overnight. It was then poured in 100 ml. water, extracted with ether and the ether solution washed with water, sodium bicarbonate solution, water and brine and dried over molecular sieves. 17.0 g. of crude product was recovered, $n_D^{25}=1.4416$, purity 99.1% of cis/trans-1-(4'-methylcyclohexyl)-1-ethyl isobutyrate. This product was distilled through a short Vigreux-column:

b.p. 28—56°C./0.35 mm., $n_D^{25}=1.4334$, 1.6 g. (Fraction 1)
b.p. 56—58°C./0.35 mm., $n_D^{25}=1.4415$, 14.2 g. (Fraction 2)

Fraction 2, the product, is 100% pure by GLC.

Example 26

cis/trans-1-(4'-Methylcyclohexyl)-1-Ethyl n-Butyrate

Using a procedure similar to Example 15, 1-(4'-methylcyclohexyl)-1-ethanol was reacted with n-butyryl chloride to form 1-(4'-methylcyclohexyl)-1-ethyl n-butyrate, b.p. 69°C./0.5 mm., $n_D^{25}=1.4455$.

Example 27

cis/trans-1-(4'-Ethylcyclohexyl)-1-Ethyl Acetate

15.6 g. (0.1 moles) of 1-(4'-ethylcyclohexyl)-1-ethanol, 11.2 g. (0.11 moles) acetic anhydride and 100 mg. p-toluene sulfonic acid were reacted and the product was recovered as described in Example 14. 18.9 g. of crude material was obtained, $n_D^{22}=1.4476$. GLC: practically pure, mixture of two isomers in 1:1 ratio of cis/trans-1-(4'-ethylcyclohexyl)-1-ethyl acetate. This material distilled at 65—70°C./0.8 mm., $n_D^{25}=1.4474$.

Example 28

cis/trans-1-(4'-Isopropylcyclohexyl)-1-Ethyl Acetate

To a mixture of 8.5 g. cis/trans-(4'-isopropylcyclohexyl)-1-ethanol and 5.5 g. (0.055 moles, 10% excess) acetic anhydride was added a few crystals of p-toluene sulfonic acid and the mixture reacted and the product was recovered as described in Example 4. Distillation through a short Vigreux-column afforded 9.4 g. product as a colorless liquid, b.p. 72°C./0.15 mm., $n_D^{24}=1.4506$. GLC showed the two stereoisomers in about equal amounts (4:6). Purity 99.3% of cis/trans-1-(4'-isopropylcyclohexyl)-1-ethyl acetate having an animal, musky, woody odor.

Example 29

cis/trans-1-(4'-Isopropylcyclohexyl)-1-Ethyl n-Butyrate

Using a procedure similar to Example 15, 1-(4'-isopropylcyclohexyl)-1-ethanol was reacted with n-butyryl chloride to form 1-(4'-isopropylcyclohexyl)-1-ethyl n-butyrate, b.p. 99°C./0.8 mm., $n_D^{25}=1.4519$.

Example 30

cis/trans-1-(4'-Tert. Butylcyclohexyl)-1-Ethyl Acetate

12.3 g. cis/trans-1-(4'-tert. butylcyclohexyl)-1-ethanol (0.0667 moles) were acetylated with 7.5 g. (0.0734 moles) of acetic anhydride and 100 mg. p-toluene sulfonic acid and the product was recovered as described in Example 14. 14.5 g. of crude product, purity 99+ % cis/trans-1-(4'-tert. butylcyclohexyl)-1-ethyl acetate by GLC, were

obtained. This colorless fragrant liquid had $n_D^{25}=1.4526$. Traces of low boilers were removed by takeover distillation. b.p. $87^\circ\text{C}/0.9\text{ mm.}$, $n_D^{25}=1.4530$.

Example 31

2-Cyclohexyl-2-Propyl Formate

A mixed anhydride reagent was prepared by adding dropwise with stirring, at 40°C. , 10.1 g. (0.22 moles) formic acid (97%) to 22.5 g. (0.22 moles) acetic anhydride containing 50 mg. p-toluene sulfonic acid. After stirring for one hour at 40°C. , 28.4 g. of 2-cyclohexyl-2-propanol were added. IR and GLC analysis showed that the reaction was quite rapid and practically complete after one hour and almost no hydrocarbons had formed. 29.2 g. of crude product, 2-cyclohexyl-2-propyl formate, was recovered ($n_D^{25}=1.4560$ (a mixture of the formate and acetate). It was distilled through a Holtzmann-column and the following fractions were taken:

b.p. $46-53^\circ\text{C.}/10\text{ mm.}$, $n_D^{25}=1.4580$ 11.0 g. (Fraction 1)

b.p. $53-56^\circ\text{C.}/10\text{ mm.}$, $n_D^{25}=1.4570$ 10.6 g. (Fraction 2)

b.p. $56^\circ\text{C.}/10\text{ mm.}$, $n_D^{25}=1.4540$ 5.8 g. (Fraction 3)

GLC analysis of the fractions showed that practically no significant separation had been achieved.

Example 32

2-Cyclohexyl-2-Propyl Acetate

21.3 g. recovered 2-cyclohexyl-2-propanol were dissolved in 20.0 g. acetic anhydride and 500 mg. 85% phosphoric acid added. Monitoring by IR showed that all of the alcohol had reacted overnight. 20 ml. water and 1.0 g. anhydrous sodium acetate were added and the mixture stirred at room temperature for one hour to hydrolyze excess acetic anhydride. Then it was poured into cold water, extracted with ether and the ether solution backwashed with water, sodium bicarbonate solution and brine and evaporated on a rotary evaporator to give 19.3 g. of crude material which analyzed by GLC to 23% mixture of two hydrocarbons and 76% of 2-cyclohexyl-2-propyl acetate. It was distilled through a Holtzmann-column:

b.p. $27^\circ\text{C.}/0.5\text{ mm.}$, $n_D^{25}=1.4600$ 2.0 g. (Fraction 1)

b.p. $42^\circ\text{C.}/0.1\text{ mm.}$, $n_D^{25}=1.4505$ 14.3 g. (Fraction 2)

Fraction 2 was 99% of the desired product by GLC. NMR analysis confirmed its structure.

Example 33

2-Cyclohexyl-2-Propyl Propionate

A mixture of 28.4 g. 2-cyclohexyl-2-propanol (0.2 moles) 39.0 g. propionic anhydride (0.3 moles) and 22.3 g. (0.22 moles) triethyl amine were heated with stirring to 120°C. and the progress of reaction monitored by GLC. After 7 hours almost all of the alcohol had been consumed and the reaction mixture was left at room temperature overnight. It then was poured into excess water and the organic layer separated. The aqueous layer was extracted with benzene, the benzene extract combined with the organic layer and thoroughly washed with water, 3% hydrochloric acid, water, sodium bicarbonate solution, water and finally with brine. The solvent was removed on a rotary evaporator at 30 mm. pressure and 50°C. bath temperature. 38.6 g. of crude product, $n_D^{25}=1.4475$, were obtained and distilled through a short Vigreux-column:

b.p. up to $69^\circ\text{C.}/0.7\text{ mm.}$, $n_D^{25}=1.4210$ 1.9 g. (Fraction 1)

b.p. up to $62^\circ\text{C.}/0.35\text{ mm.}$, $n_D^{25}=1.4504$ 32.2 g. (Fraction 2)

The product is 96.8% pure 2-cyclohexyl-2-propyl propionate by GLC, impurity is unreacted 2-cyclohexyl-2-propanol (GLC analysis). The product is a colorless, mobile liquid with a chemical, camphoraceous odor.

Example 34

2-Cyclohexyl-2-Propyl Isobutyrate

A mixture of 28.4 g. (0.2 moles) 2-cyclohexyl-2-propanol 40.0 g. (0.25 moles) isobutyric anhydride and 22.3 g. (0.22 moles) triethyl amine was heated to reflux overnight and the product was recovered as described in Example 33 to give 42.7 g. of a crude product, $n_D^{25}=1.4442$. Distillation through a short Vigreux-column afforded:

b.p. $43^\circ\text{C.}/0.5-60^\circ\text{C.}/0.3\text{ mm.}$, $n_D^{24}=1.4278$, 8.5 g. (Fraction 1)

b.p. $70^\circ\text{C.}/0.7\text{ mm.}$, $n_D^{24}=1.4475$, 33.0 g. (Fraction 2)

Fraction 1 contained unreacted and unhydrolyzed isobutyric anhydride. The product was 98.7% (GLC analysis) pure 2-cyclohexyl-2-propyl isobutyrate. The product was a colorless, mobile liquid with a floral, citrus, rose muguet odor.

Example 35

2-Cyclohexyl-2-Propyl n-Butyrate

To a solution of 28.4 g. (0.2 moles) 2-cyclohexyl-2-propanol and 24.0 g. (0.3 moles) pyridine in 100 ml. anhydrous ether, chilled in an ice-salt bath, was added with stirring a solution of 23.4 g. (0.22 moles) freshly redistilled butyryl chloride at such a rate as to keep the temperature around 0°C. The ice bath was removed after complete addition and stirring continued for two hours. Then the solid was dissolved in the minimum amount of water and the organic layer separated. It was washed with water, 3% hydrochloric acid, water, sodium bicarbonate solution, water again and finally with brine. After drying over molecular sieves overnight a crude product (42.0 g.) was recovered, $n_D^{25}=1.4603$. This product contained unreacted alcohol as a major impurity. Distillation through a short Vigreux-column afforded:

b.p. up to 67°C./0.25 mm., $n_D^{25}=1.4548$ 4.5 g. (Fraction 1) mostly low boilers

b.p. 67—71°C./0.2 mm., $n_D^{25}=1.4522$ 27.2 g. (Fraction 2) mostly product

Fraction 2 was redistilled:

b.p. 48—60°C./0.1 mm., $n_D^{25}=1.4572$ 5.3 g. Fraction 2A)

b.p. 60°C./0.1 mm., $n_D^{25}=1.4514$ 20.8 g. (Fraction 2B)

Fraction 2B was analyzed by GLC to 99.9% purity 2-cyclohexyl-2-propyl n-butyrate. The product was a colorless, mobile liquid with a chemical, fruity odor.

Example 36

The following malodor concentrate was prepared:

Bathroom Malodor Concentrate

Component	Parts by Wt.
skatole	0.91
β -thionaphthol	0.91
95% aqueous solution of thioglycolic acid	21.18
n-caproic acid	6.00
p-cresyl isovalerate	2.18
N-methyl morpholine	6.00
dipropylene glycol	62.82

Aerosol cans were prepared with the above malodor with the following concentrations:

Bathroom Malodor Aerosol

Component	Parts by Wt.
Bathroom Malodor Concentrate	0.1
dipropylene glycol	4.9
Propellant	
a. trichloromonofluoromethane	47.5
b. dichlorodifluoromethane	47.5

A "Spice for Cologne" fragrance was selected for use in testing the malodor counteractant ability of the compounds tested. The "Spice for Cologne" fragrance contained the following ingredients:

	Ingredients	Parts by Wt.	
	Lavandin Abrialis Oil	60	
	Amyl Cinnamic Aldehyde	20	
	Amyl Salicylate	150	
5	Benzyl Acetate	30	5
	Linalool	30	
	Cedarwood Oil	10	
	Geraniol	130	
	Isopulegol	60	
10	Methyl Anthranilate (10% by weight solution in dipropylene glycol)	20	10
	Musk Xylol	60	
	Coumarin	50	
	Phenyl Ethyl Acetate	30	
	Terpinyl Acetate	100	
15	Cinnamon Leaf Oil	40	15
	Petitgrain Oil SA	60	
	Ylang ylang Oil	130	
	Phenyl Acetaldehyde Dimethyl Acetal	15	
	Cinnamic Alcohol	5	
20		1000	20

Aerosol cans were prepared with the above fragrance composition with and without 1-cyclohexyl-1-ethyl n-butyrate being present as a malodor counteractant as follows:

	Without 1-cyclohexyl-1-ethyl n-butyrate		
25	"Spice for Cologne" fragrance	% by Wt.	25
	Propellant	0.5	
	a. trichloromonofluoromethane	49.75	
	b. dichlorodifluoromethane	49.75	
30		100.00	30
	With 1-cyclohexyl-1-ethyl n-butyrate		
	"Spice for Cologne" fragrance	0.45	
	1-cyclohexyl-1-ethyl n-butyrate	0.05	
	Propellant		
35	a. trichloromonofluoromethane	49.75	35
	b. dichlorodifluoromethane	49.75	
		100.00	

A test chamber having inside dimensions of $3.35 \times 3.66 \times 2.44$ (meters) with a total volume of 29.9 cubic meters, having an access door and an exhaust fan was provided. The capacity of the exhaust fan was 14 cubic meters/min. In order to improve satisfactory evacuation the exhaust fan was operated for five minutes between tests and an olfactory check was made to determine if any residual odor could be detected prior to conducting the next test.

After the test chamber had been suitably evacuated the bathroom malodor was sprayed from the aerosol can for about five seconds. After a delay of from 10—15 seconds the fragrance composition aerosol was sprayed for about five seconds (five seconds being an average time such an aerosol would usually be used by a housewife). One minute thereafter a 2 member panel (consisting of 1 person skilled in perfumery and odor evaluation and 1 person having no such skills but being familiar with fragrances in general) entered the test chamber, performed an olfactory evaluation for detection of the malodor and recorded their observations. All tests were performed with neither member of the panel being aware of the identity of the material being tested.

Based on the flow rate through the valve utilized in the aerosol can the approximate amount of aerosol, containing the malodor concentrate, introduced into the test chamber is:

Aerosol Containing Malodor Concentrate Bathroom	Amount (mg./cu.meter) 267
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The amount of aerosol containing the fragrance compositions introduced into the test chamber is approximately 260 mg./cu. meter.

When the above described test procedure was carried out using the "Spice for Cologne" fragrance composition aerosol with 1-cyclohexyl-1-ethyl n-butyrate neither member of the panel could detect the presence of the malodor. This is a particularly surprising result because when the "Spice for Cologne" fragrance composition aerosol without 1-cyclohexyl-1-ethyl n-butyrate is tested both members of the panel detected the presence of the malodor. The panel commented that the malodor counteractant effect was outstanding and that there was produced a fresh air effect (FAE), real ozone effect, with a very nice and low residual odor from the compound tested.

Example 37

An aerosol can was prepared with the following concentrations:

Component	Parts by Wt.
1-cyclohexyl-1-ethyl n-butyrate	0.05
Propellant	
a. trichloromonofluoromethane	49.975
b. dichlorodifluoromethane	49.975

The aerosol was utilized in the above-described test procedure (aerosol—267 mg./cu. meter). Neither member of the panel could detect the presence of the malodor. However, 1-cyclohexyl-1-ethyl n-butyrate is not particularly pleasing in its odor properties when used alone.

Example 38

The exemplary compounds indicated in Table 1 were incorporated into "Spice for Cologne" fragrance composition aerosol cans according to the procedures of Example 36 and, using the test procedures of Example 36, they were tested for their ability to counteract the bathroom malodor. The results are shown in Table 1.

Compound of Ex.	Activity*	Comments	
1	U	FAE**, very clean, light background	
2	U	FAE, clean, fresh and light background	
3	U	FAE, very clean, lighter, fruity note in residual	30
4	U*	FAE, very clean, ozone-like freshness, very light residual	
5	V	No malodor, clean, but muted and unappealing background odor quality	
6	V	No malodor, clean, but blends badly and seems to act slower	
7	U*	FAE, very clean and extremely light and fresh	35
8	V	No malodor, light residual with a spicy note	
9	U	FAE, very clean, very nice and fresh, low residual	
10	U	FAE, very clean, fresh and low residual	
12	WV	No malodor, stronger residual odor	
13	U*	FAE, almost no residual odor	40
14	VU	No malodor, weak FAE, residual background	
15	WV	No malodor, no FAE, pungent and irritating background	
16	V	No malodor, medium background, some irritation	
17	W	Slight malodor, poor activity, heavy residual odor, no synergistic effect, perhaps slower and longer lasting	45
18	VU	No malodor, weak FAE, but very fresh residual background	
19	V	gistic effect, perhaps slower and longer lasting	
20	VU	No FAE, no malodor, highly perfumed residual odor, perhaps slower and longer acting	50
21	U	No malodor, weak FAE, somewhat heavier residual background odor	
22	VU	FAE, clean, fresh, light residual	
23	U*	No malodor, weak FAE, less fresh and heavier residual background odor	55
24	U	FAE, very clean, extremely light background, longer lasting than usual	
25	VU	FAE, very light residual odor, light fragrance in background	
26	W	Slightly pungent, but clean and no residual malodor	
27	U	Trace of malodor in background, flat residual odor, no apparent malodor counteractant contribution	60
		FAE, light and fresh residual odor	

Compound of Ex.	Activity	Comments	
28	U	FAE, fresh and clean	
29	U	FAE, pleasant, light background and residual odor	
30	V	No malodor, clean, but heavy residual background odor	
5 31	U	FAE, fresh, almost irritating, clean and acceptable residual odor intensity	5
32	VU	FAE, slower action but very clean, fresh and light residual	
33	VU	Borderline excellent, FAE slow, no sharp impact, no malodor, clean acceptable residual	
10 34	U	FAE, clean and nice residual	10
35	U	FAE, clean and nice residual of lower intensity	
acetate (4'-methylcyclohexyl)-2-propyl cis/trans-2-	X	No malodor, but medium heavy residual, poor mix with fragrance, unpleasant	15

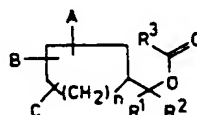
* Ability of compound to counteract the malodor according to the following scale:

	U*	"Outstanding"—Fresh air effect pronounced and producing extremely light or no residual odor at all.	
20	U	"Excellent"—Fresh air effect and light and pleasant residual background odor.	20
	V	"Very good"—No fresh air effect but total abatement of malodors, variable, but not high residual background odor.	
25	W	"Good"—Only traces of malodor, often of changed quality, remain. Residual background odor acceptable to pleasant, not too strong.	25
	X	"Fair"—Original malodor clearly discernable but of low intensity. Residual background odor acceptable at best.	
30	Y	"Poor"—Original malodor somewhat reduced in intensity, but dominates. Overall residual background odor unpleasant to unacceptable.	30
	Z	"No activity".	

** FAE—fresh air effect.

WHAT WE CLAIM IS:—

- 35 1. A composition to be used to counteract malodors wherein an amount, effective to counteract the malodor, of an ester represented by the structural formula



wherein

- 40 n is an integer of from 1 to 4,
 A, B and C each independently represent hydrogen or an alkyl group having from 1 to 5 carbon atoms, each such alkyl group, when there are more than one, being attached to a different carbon atom of the ring, provided that the sum of the carbon atoms, in A, B and C is no more than 7,
 45 R¹ and R² each independently represent hydrogen or an alkyl group having from 1 to 5 carbon atoms or R¹ and R² taken together represent $-(CH_2)_m-$ wherein m is an integer of from 2 to 6, provided that when both R¹ and R² represent hydrogen, (a) each of A, B and C represents hydrogen, or (b) A represents tert-butyl and B and C each represent hydrogen,
 50 R³ represents hydrogen or an alkyl group having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R¹ or R² plus R³ is no more than 10, is present in the composition.
2. A composition according to Claim 1 wherein the malodor counteractant ester is present in an amount sufficient to provide at least about 0.01 mg./cu. meter of air containing the malodor.
- 55 3. A composition according to Claim 1 which is a room freshener.
4. A composition according to any of Claims 1 to 3 comprising a said ester and an aerosol propellant.
5. A composition according to any of Claims 1 to 3 comprising a said ester and a wax, plastics material, powder or gel.

6. A composition according to any of Claims 1 to 3 comprising a said ester and a surface active agent, or disinfectant.

7. A composition according to any of Claims 1 to 3 comprising a said ester on a fibrous substrate.

8. A composition according to any of Claims 1 to 7 containing a fragrance component.

9. A composition according to any of Claims 1 to 5 wherein n is 2.

10. A composition according to Claim 9 wherein the malodor counteractant is cyclohexylmethyl propionate, cyclohexylmethyl isobutyrate, cyclohexylmethyl n-butyrate, cis/trans-4-tert-butylcyclohexylmethyl acetate, 1-cyclohexylethyl formate, 1-cyclohexylethyl propionate, 1-cyclohexylethyl isobutyrate, 1-cyclohexylethyl n-butyrate, cis/trans-1-(2'-methylcyclohexyl)ethyl n-butyrate, cis/1-cyclohexylpropyl n-butyrate, cis/trans-1-(4'-methylcyclohexyl)ethyl n-butyrate, cis/trans-1-(4'-ethylcyclohexyl)ethyl acetate, cis/trans-1-(4'-isopropylcyclohexyl)ethyl acetate, cis/trans-1-(4'-isopropylcyclohexyl)ethyl n-butyrate, 2-cyclohexylpropyl formate, 2-cyclohexylpropyl isobutyrate or 2-cyclohexylpropyl n-butyrate.

11. A composition according to Claim 4 substantially as described in any one of Examples 36, 37 and 38.

12. A method of treating malodors to alleviate their offensive odors which comprises treating the air containing the malodor with an amount, effective to counteract the malodor, of an ester as defined in Claim 1.

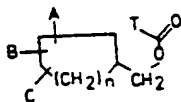
13. A method according to Claim 12 wherein the malodor counteractant compound is provided in an amount sufficient to provide at least 0.01 mg./cu. meter of air containing the malodor.

14. A method according to either of Claims 12 and 13 wherein the malodor counteractant compound is utilized in the form of a room freshener.

15. A method according to Claim 14 wherein the room freshener is introduced as an aerosol.

16. A method according to any of Claims 12 to 15 wherein the ester is any of those specified in Claim 10.

17. A compound represented by the structural formula



wherein

n is an integer of from 1 to 4,

A, B and C each represent hydrogen and

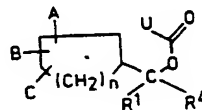
T represents an alkyl group having from 3 to 6 carbon atoms.

18. A compound according to Claim 17 wherein n is 2.

19. A compound according to Claim 18 which is cyclohexylmethyl isobutyrate.

20. A compound according to Claim 18 which is cyclohexylmethyl n-butyrate.

21. A compound represented by the structural formula



wherein

n is an integer of from 1 to 4,

A, B and C each independently represent hydrogen or an alkyl group having from 1 to 5 carbon atoms, each such alkyl group, when there are more than one, being attached to a different carbon atom of the ring provided that the sum of the carbon atoms in A, B and C is no more than 7,

R¹ represents hydrogen or an alkyl group having from 1 to 5 carbon atoms,

R⁴ represents an alkyl group having from 1 to 5 carbon atoms or R¹ and R⁴ taken together represent $-(CH_2)_m-$ wherein m is an integer of from 2 to 6, and

U represents hydrogen or an alkyl group having from 2 to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R¹ or R⁴ plus U is no more than 10.

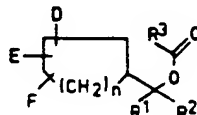
22. A compound according to Claim 21 wherein n is 2.

23. A compound according to Claim 22 which is 1-cyclohexyl-1-ethyl formate.

24. A compound according to Claim 22 which is 1-cyclohexyl-1-ethyl propionate.

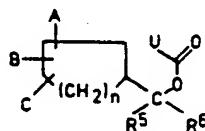
25. A compound according to Claim 22 which is 1-cyclohexyl-1-ethyl isobutyrate.

26. A compound according to Claim 22 which is 1-cyclohexyl-1-ethyl n-butyrate.
 27. A compound according to Claim 22 which is 1-cyclohexyl-1-propyl n-butyrate.
 28. A compound according to Claim 22 which is cis/trans-1-(2'-methylcyclohexyl)-1-ethyl n-butyrate.
 29. A compound according to Claim 22 which is cis/trans-1-(3'-methylcyclohexyl)-1-ethyl n-butyrate.
 30. A compound according to Claim 22 which is cis/trans-1-(4'-isopropylcyclohexyl)-1-ethyl n-butyrate.
 31. A compound represented by the structural formula



wherein

- n is an integer of from 1 to 4,
 R¹ and R² each independently represent hydrogen or an alkyl group having from 1 to 5 carbon atoms or R¹ and R² taken together represent $-(CH_2)_m-$ wherein m is an integer of from 2 to 6,
 R³ represents hydrogen or an alkyl group having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R¹ or R² plus R³ is no more than 10, and
 D, E and F each independently represent hydrogen or an alkyl group having from 2 to 5 carbon atoms, each such alkyl group, when there are more than one, being attached to a different carbon atom of the ring, provided that at least one of D, E or F is not hydrogen, that when both R¹ and R² represent hydrogen, D represents tert-butyl and E and F each represent hydrogen, and that the sum of the carbon atoms in D, E and F is no more than 7.
 32. A compound according to Claim 31 wherein n is 2.
 33. A compound according to Claim 32 which is cis/trans-4-tert-butylcyclohexyl-methyl acetate.
 34. A compound according to Claim 32 which is cis/trans-1-(4'-ethylcyclohexyl)-1-ethyl acetate.
 35. A compound according to Claim 32 which is cis/trans-1-(4'-isopropylcyclohexyl)-1-ethyl acetate.
 36. A compound represented by the structural formula



wherein

- n is an integer of from 1 to 4,
 A, B and C each independently represent hydrogen or an alkyl group having from 1 to 5 carbon atoms, each such alkyl group, when there are more than one, being attached to a different carbon atom of the ring, provided that the sum of the carbon atoms in A, B and C is no more than 7,
 U represents hydrogen or an alkyl group having from 2 to 6 carbon atoms, and
 R⁵ and R⁶ each independently represent an alkyl group having from 1 to 5 carbon atoms or R⁵ and R⁶ taken together represent $-(CH_2)_m-$ wherein m is an integer of from 2 to 6, provided that the sum of the larger number of carbon atoms in R⁵ or R⁶ plus U is no more than 10.
 37. A compound according to Claim 36 wherein n is 2.
 38. A compound according to Claim 37 which is 2-cyclohexyl-2-propyl formate.
 39. A compound according to Claim 37 which is 2-cyclohexyl-2-propyl isobutyrate.
 40. A compound according to Claim 37 which is 2-cyclohexyl-2-propyl n-butyrate.

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